Designation: D 4646 – 03

Standard Test Method for
24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments[1]

1. Scope

1.1 This test method describes a procedure for determining the sorption affinity of waste solutes by unconsolidated geologic material in aqueous suspension. The waste solute may be derived from a variety of sources such as wells, underdrain systems, or laboratory solutions such as those produced by waste extraction tests like the Test Method D 3987 shake extraction method.

1.2 This test method is applicable in screening and providing relative rankings of a large number of geomedia samples for their sorption affinity in aqueous leachate/geomedia suspensions. This test method may not exactly simulate sorption characteristics that would occur in unperturbed geologic settings.

1.3 While this procedure may be applicable to both organic and inorganic constituents, care must be taken with respect to the stability of the particular constituents and their possible losses from solution by such processes as degradation by microbes, light, or hydrolysis. This test method should not be used for volatile chemical constituents (see 6.1).

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]
D 1129 Terminology Relating to Water
D 1193 Specification for Reagent Water
D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock

D 3987 Test Method for Shake Extraction of Solid Waste with Water
D 4319 Test Method for Distribution Ratios by the Short-Term Batch Method

3. Terminology

3.1 *Definitions*—For definition of terms used in this test method refer to Terminology D 1129.

3.1.1 *solute*—chemical species (for example, ion, molecule, etc.) in solution.

3.1.2 *sorbate*—chemical species sorbed by a sorbent.

3.1.3 *sorbent*—a substance that sorbs the solute from solution (for example, soil, sediment, till, etc.).

3.1.4 *sorption*—depletion of an amount of solute initially present in solution by a sorbent.

3.1.5 *sorption affinity*—the relative degree of sorption that occurs by a geomedia.

3.1.6 *unconsolidated geologic material (geomedia)*—a loosely aggregated solid natural material of geologic origin (for example, soil, sediment, till, etc.).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *distribution coefficient, K_d*—the ratio of the concentration of solute sorbed on the soil or other geomedia divided by its concentration in solution. A 24-h K_d is the analogous ratio evaluated after 24 h of contact of the solute with the geomedia.

3.2.1.1 *Discussion*—The dimensions of K_d reduce to units of volume per mass. It is convenient to express K_d in units of millilitres (or cubic centimetres) of solution per gram of geomedia. Dissimilar K_d values may be obtained if different initial solute concentrations are used, depending on the sorption behavior of the solute and the properties of the geomedia (that is, nonlinear sorption curve). This concentration dependency may be absent where the solute concentrations are sufficiently low or the characteristics of the particular solute-sorbent combination yield K_d values that are independent of the concentration of solute (that is, linear sorption curve).

4. Summary of Test Method

4.1 Distilled water, natural water, waste leachate, or other aqueous solution containing a known concentration of a solute is mixed with a known amount of unconsolidated geologic

material (geomedia) for 24 h. After 24 h, equilibrium between the solid and solution phase is presumed to occur. The concentration of solute remaining in solution is measured and the amount of solute adsorbed is calculated. Given that the mass of solid phase is known, the distribution coefficient for the specified experimental conditions can then be calculated.

5. Significance and Use

5.1 This test method is meant to allow for a rapid (24 h) index of a geomedia's sorption affinity for given chemicals or leachate constituents. A large number of samples may be run using this test method to determine a comparative ranking of those samples, based upon the amount of solute sorbed by the geomedia, or by various geomedia or leachate constituents. The 24-h time is used to make the test convenient and also to minimize microbial degradation which may be a problem in longer-timed procedures. While K_d values are directly applicable for screening and comparative ranking purposes, their use in predictive field applications generally requires the assumption that K_d be a fixed value.

5.2 While this test method may be useful in determining 24-h K_d values for nonvolatile organic constituents, interlaboratory testing has been carried out only for the nonvolatile inorganic species, arsenic and cadmium. However, the procedure has been tested for single laboratory precision with polychlorinated biphenyls (PCBs) and is believed to be useful for all stable and nonvolatile inorganic, and organic constituents. This test method is not considered appropriate for volatile constituents.

5.3 The 24-h time limit may be sufficient to reach a steady-state K_d. However, to report this determination as a steady-state K_d, this test method should be conducted for intermediate times (for example, 12, 18 and 22 h) to ensure that the soluble concentrations in the solution have reached a steady state by 24 h. Refer to Test Method D 4319 for an alternate procedure of longer duration.

6. Interferences

6.1 When dealing with solutes of unknown stability either in contact with the geomedia or when used as blanks, care must be taken to determine if volatilization, hydrolysis, photodegradation, microbial degradation, oxidation-reduction (for example, Cr^{3+} to Cr^{6+}) or other physicochemical processes are operating at a significant rate within the time frame of the procedure. The stability and hence loss from solution may affect the outcome of this procedure if the aforementioned reactions are significant. The compatibility of the method and the solute of interest may be assessed by determining the differences between the initial solute concentration (see 9.8) and the final blank concentration of the solute (see 9.15). If this difference is greater than the expected precision of the method (10 %), then the K_d value generated may be unreliable and must be carefully evaluated.

7. Apparatus

7.1 *Agitation Equipment*—The agitation equipment to be used is the rotary solid waste extractor[3] specified in Test Method D 3987.

7.2 *Phase Separation Equipment*—A filtration apparatus made of materials compatible with the solutions being filtered and equipped with a 0.45-μm pore size membrane filter, or a constant temperature centrifuge capable of separating particles with diameters greater than 0.1 μm (see Section 9). If organic compounds are being measured, the filtration apparatus, centrifuge tubes etc., should be compatible with the compounds being measured (that is, glass or stainless steel). Sorption of solute onto the filtration membrane may be significant for some solutes, and must be evaluated by the use of blanks through all steps of the procedure.

7.3 *Containers*—Round, wide-mouth bottles compatible with the rotary extractor (Test Method D 3987) and of composition suitable to the nature of the solute(s) under investigation and the analysis to be performed will be used. For nonvolatile inorganic constituents, high-density, linear polyethylene bottles should be used with the size of the bottle dictated by sample size, and the need for the solution to occupy 70 to 80 % of the container volume (that is, 125 mL, 250 mL, or 2-L bottles for sample sizes of 5, 10, or 70 g respectively). For nonvolatile organic constituents, TFE-fluorocarbon, glass bottles, or stainless steel containers with water-tight closures made of chemically inert materials should be used with size requirements being the same as for nonvolatile inorganics. Containers should be cleaned in a manner consistent with the analyses to be performed. Samples of the solutions to be analyzed should be stored in similar chemically compatible bottles.

7.4 *Balance*, having a minimum capacity of 70 g and a sensitivity of ±0.005 g shall be used.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water of Specification D 1193.

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[3] Diamondstone, B. T., Burke, R. W., and Garner, E. L., "Improved Leach Measurements on Solid Wastes," *ASTM Standardization News*, June 1982, pp. 28–33.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

9. Procedure

9.1 Geomedia samples are spread out on a flat surface, no more than 2 to 3 cm deep, and allowed to air dry for 7 days or until constant weight (a change that is less than 5 %/24-h period) is achieved (do *not* oven dry).

9.2 After the sample has air dried, it is passed through a 2-mm screen sieve. Large aggregates are to be crushed, without grinding, using a clean mortar and a rubber-tipped pestle.

9.3 Mix the sieved material until the sample is homogeneous. Use a riffle splitter, or other unbiased splitting procedure, to obtain subsamples of appropriate size.

9.4 Remove subsamples and determine the moisture content of the air-dried sample (refer to Test Method D 2216).

9.5 Determine the mass of geomedia sample, corrected for moisture content:
Determination of air-dried soil mass equivalent to the desired mass of oven-dried soil:

$$A = M_s[1 + (M/100)] \qquad (1)$$

where:
A = air dry soil mass
M_s = mass of oven-dried soil desired, and
M = moisture, %.

9.6 Place between 5 and 70 g (oven-dried basis) of the weighed air-dried sample into the appropriate container. The samples should be weighed to a minimum of three significant figures.

9.7 Add to the container an amount of solute solution necessary to yield a 1:20 soil-to-solution ratio. This is determined on the oven-dried basis:
Determination of solution volume needed per sample for a soil-to-solution ratio of 1:20:

$$V = (M_s \times 20)/\rho \qquad (2)$$

where:
ρ = density of solution, g/cm^3,
V = volume of solution per sample, cm^3, and
M_s = mass of soil to be used, g, (oven-dried basis).

9.8 Retain a separate, appropriately preserved aliquot of the initial solute solution for analysis.

9.9 Close the container and place it on the rotary extractor (Test Method D 3987).

9.10 Agitate continuously for 24 ± 0.5 h at 29 ± 2 r/min at room temperature (22 ± 5°C).

9.11 Open the container. Note the temperature of the solution and any changes in the sample or solution (that is, color, odor, etc.).

9.12 Separate the solution phase from the majority of the solid phase by decantation.

9.13 Filter the solution phase through a 0.45-μm pore size membrane filter (see 7.2), or centrifuge a subsample at the predetermined rate of rotation and time for the centrifugation equipment employed at constant temperature (the temperature recorded after 24 h):

$$t = 9/2 \left(\frac{\eta}{\omega^2 r_p{}^2 (\rho_p - \rho)} \right) \ln (R_b/R_t) \qquad (3)$$

where:
$$\omega^2 = \frac{4\pi^2 (r/min)^2}{60}$$

= angular velocity,
r_p = particle radius, cm,
η = viscosity of water, 8.95×10^{-3} g/s-cm at 25°C,
ρ_p = particle density,
ρ = density of solution,
r/min = revolutions per minute,
R_t = distance from center of centrifuge rotor to top of solution in centrifuge tube, cm,
R_b = distance from center of centrifuge rotor to bottom of centrifuge tube, cm, and
t = time, min.

To remove particles >0.1-μm radius and 2.65-g/cm^3 density from solution:

$$t = \left(\frac{3.71 \times 10^8}{(r/min)^2} \right) \ln (R_b/R_t) \qquad (4)$$

Note that if filtration is used, the affinity of the filtration membrane for the solute must be evaluated. Failure to do so may lead to erroneous results.

9.14 After a clear solution has been obtained, place an aliquot in an appropriate container (see 7.3), and analyze or store in a refrigerator at 4 ± 2°C until analyzed.

9.15 Each geomedia sample is to be subjected to the procedure in three or more replicates. The number of blanks (that is, solute solution without geomedia) carried through all steps of the procedure should be a minimum of 5 % of the total number of geomedia samples, but not less than three.

10. Calculation

10.1 Calculate the distribution as follows:

$$K_d = \frac{(A - B)V}{(M_s)B} \qquad (5)$$

where:
A = initial concentration of the solute defined as the mean concentration of the blanks, μg/mL,
B = final concentration of the solute after 24 h in contact with the geomedia, μg/mL,
V = volume of solution used, mL,
M_s = mass of soil expressed on an oven-dried basis, g, and
K_d = distribution coefficient, mL/g.

11. Report

11.1 The K_d value must be clearly marked as nonequilibrium 24-h distribution coefficient.

11.2 Both the initial solute concentration (A in 10.1) and the final solute concentration (B in 10.1) must be reported.

11.3 The initial and final solute concentration for each blank (solution without geomedia) must be reported.

11.4 The mass of the sorbent (M_s in 10.1), volume of solution (V in 10.1), and the room temperature at which the rotary extractor was operated must be reported.

11.5 Report the temperature of the solution and any changes noted in 9.11.

11.6 Note and report negative K_d values when and if they occur. Negative K_d values may occur if the geomedia contains the test solute prior to the application of the method.

11.7 It is suggested that the pH of the sorbent-solute mixture be determined prior to separating the sorbent from the liquid and reported where feasible.

12. Precision and Bias

12.1 An interlaboratory round-robin test was conducted at a soil-to-solution ratio of 1:20 using 70.0 g of soil. Intralaboratory testing using a 1:20 soil-to-solution ratio was carried out with no significant loss of precision for soil masses of 5.00, 10.0, and 70.0 g. Therefore, it is specified that the soil-to-solution ratio be 1:20 with the working mass of soil (on an oven-dried basis) between 5 and 70 g.

12.2 *Precision*:

12.2.1 The precision of this test method is limited by the ability to obtain a homogeneous sample of geomedia, and the precision of the various methods used to carry out the procedure (that is, mass determinations, initial and 24-h concentration of constituents).

12.2.2 A comprehensive overall precision statement, covering all species, is not feasible. Interlaboratory testing of this procedure, using cadmium and arsenic as sorbates, with five independent laboratories, and single laboratory testing with PCBs indicated that a coefficient of variation of less than 10 % is obtainable.

12.2.3 For a summary of interlaboratory testing for the 24-h batch-type K_d determination see Table 1.

12.2.4 For a summary of single laboratory testing for an organic solute see Table 2.

12.3 *Bias*—A determination of the bias for this procedure is not possible since no standard soil or alternate technique exists.

TABLE 1 Summary of Interlaboratory Testing for the 24-h Batch-Type K_d Determination

Initial Concentration, µg/mL	Soil 1	Soil 1	Soil 2	Soil 3	Soil 4
	10	200	100	100	100
Cadmium Carbonate (as CdCO₃):					
$\bar{X}$ K_d, mL/g	1568	96.3	69.50	69.74	28.94
Standard deviation, mL/g	±156	±6.32	±7.73	±7.87	±2.64
Coefficient of variation, %	9.95	6.56	11.13	11.29	9.14
Number of replicates	12	12	10	12	9
Arsenic (as KH₂AsO₄):					
$\bar{X}$ K_d, mL/g	15.42	2.75	4.95	3.25	2.99
Standard deviation, mL/g	±0.92	±0.85	±0.27	±0.26	±0.20
Coefficient of variation, %	5.99	30.9	5.53	7.88	6.52
Number of replicates	12	12	12	12	12

TABLE 2 Summary of Single Laboratory for an Organic Solute

Initial Concentration, µg/mL	Soil 1[A] 0.216 (0 % Acetone)	Soil 1[B] 0.187 (20 % Acetone)	Soil 2[C] 0.216 (0 % Acetone)	Soil 2[D] 0.187 (20 % Acetone)
PCBs (as Aroclor 1242):				
$\bar{X}$ K_d, mL/g	798	78.62	23.83	2.28
Standard deviation, mL/g	±18.41	±3.45	±1.48	±0.11
Coefficient of variation, %	2.31	4.39	6.21	4.82
Number of replicates	4	4	4	4

[A] Soil 1—Catlin silt loam.
[B] Soil 2—Sangamon paleosol.
[C] Soil 3—Kaolinite clay.
[D] Soil 4—Vandalia till, unaltered phase.